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(19) (CA) **CANADIAN PATENT** (12)

(54) **Hydroprocessing Catalyst and Method of Preparation**

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ABSTRACT

A hydrocarbon hydroprocessing catalyst containing a Group VIB metal and a phosphorus component on a porous refractory oxide is prepared by impregnating support particles with a solution containing (1) phosphorus, and (2) citric acid in a mole ratio of Group VIB metal components of less than 1 to 1, followed by drying and calcining. The catalyst is useful for promoting a number of hydrocarbon hydroprocessing reactions, particularly those involving hydrogenative desulfurization, demetallization and most particularly, denitrogenation.

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BACKGROUND OF THE INVENTIONField of the Invention

This invention relates to hydrocarbon hydroprocessing catalysts, such as those utilized to catalyze the reaction of hydrogen with organo-sulfur, organo-metallic and particularly organo-nitrogen compounds. More particularly this invention is directed to a catalyst useful for the hydrodesulfurization of hydrocarbons, such as gas oils and residuum, and to a method for preparing such catalysts by



1 employing a novel aqueous impregnating solution. The inven-
2 tion is especially directed to catalysts of high overall de-
3 nitrogenation activity and stability.

4 Description of the Prior Art

5 In the refining of hydrocarbons, it is often nec-
6 essary to convert a hydrocarbon oil fraction to different
7 forms. Typically, particulate catalysts are utilized to
8 promote desulfurization, denitrogenation or demetallization
9 reactions when feedstocks such as gas oils or residuum are
10 contacted with catalysts under conditions of elevated tem-
11 perature and pressure and in the presence of hydrogen so
12 that the sulfur components are converted to hydrogen sul-
13 fide, the nitrogen components to ammonia and the metals are
14 deposited on the catalyst.

15 Hydroprocessing of hydrocarbon oils may be carried
16 out with a catalyst containing Group VIB and Group VIII met-
17 als and phosphorus on a refractory oxide support. Composi-
18 tions containing these and other elements have been previous-
19 ly investigated. For example, catalysts comprising a Group
20 VIB metal, particularly molybdenum or tungsten, a Group VIII
21 metal, particularly cobalt or nickel, and phosphorus on an
22 alumina base have been disclosed in U.S. Patents 3,755,196,
23 3,840,472 and 4,686,030. Such catalysts are very often pre-
24 pared by impregnation, that is, the deposition of the active
25 components on the support base by contact thereof with an
26 aqueous solution containing the active components in dis-
27 solved form. U.S. Patent 3,755,196, for example, describes
28 impregnating media and methods for preparing catalysts using
29 stabilized impregnating solutions consisting of molybdenum
30 plus nickel or cobalt salts with phosphoric acid dissolved

1 in an aqueous medium. U.S. Patent 3,840,472 discloses an-
2 other process for preparing a stable impregnating solution
3 that includes dissolving a nickel or cobalt compound with an
4 acid of phosphorus followed by subsequent dissolution of mo-
5 lybdenum oxide. U.S. Patent 4,686,030 describes an impreg-
6 nating solution containing dissolved Group VIII metals and
7 dissolved molybdenum that is prepared by solubilizing mo-
8 lybdenum with either phosphoric acid, ammonium hydroxide or
9 citric acid alone.

10 Although conventional catalysts are active and
11 stable for hydrocarbon hydroprocessing reactions, catalysts
12 of yet higher activities and stabilities are still being
13 sought. Increasing the activity of a catalyst increases the
14 rate at which a chemical reaction proceeds under given condi-
15 tions, and increasing the stability of a catalyst increases
16 its resistance to deactivation, that is, the useful life of
17 the catalyst is extended. In general, as the activity of a
18 catalyst is increased, the conditions required to produce a
19 given end product, such as a hydrocarbon of given sulfur,
20 nitrogen, and/or contaminant metals content, become more
21 mild. Milder conditions require less energy to achieve the
22 desired product, and catalyst life is extended due to such
23 factors as lower coke formation or the deposition of less
24 metals.

25 26 SUMMARY OF THE INVENTION

27 Briefly, the invention provides for a catalyst
28 useful for hydroprocessing hydrocarbon oils and for a method
29 for preparing such a catalyst employing a novel impregnat-
30 ing solution. In one embodiment, an aqueous impregnating
31

solution of a pH value less than 1 is prepared containing at least one dissolved Group VIB metal component, at least one dissolved phosphorus component and citric acid, the mole ratio of the citric acid to the Group VIB metal component being greater than 0.1:1 but less than 0.5:1. A catalyst composition comprising a Group VIB metal component and a phosphorus component on a refractory oxide is prepared by impregnating support particles with this solution, followed by calcination. In a preferred embodiment, a hydroprocessing catalyst is prepared by the method of impregnating alumina-containing support particles with a stable aqueous impregnating solution having a pH less than 1 and comprising a dissolved molybdenum component, a dissolved nickel or cobalt component, an acidic compound of phosphorus and citric acid, followed by calcination. In this embodiment the solution contains (1) molybdenum components (as MoO_3) in a total concentration greater than about 10 weight percent (2) phosphorus components (as P) in a total concentration greater than about one weight percent and (3) citric acid components (as the monohydrate) in a mole ratio to the molybdenum components (as MoO_3) in the range between 0.1:1 to 0.5:1.

Catalysts prepared in accordance with the invention are useful for promoting the hydroprocessing of hydrocarbon oils, particularly by hydronitrogenation. A catalyst prepared with the impregnating solution described above exhibits high activity and stability when utilized to promote high conversions of organo-nitrogen compounds, particularly those found in hydrocarbon gas oils, to ammonia. Some of the catalysts prepared by the above-mentioned method are novel.

DETAILED DESCRIPTION OF THE INVENTION

Hydrocarbon hydroprocessing catalysts of the present invention are prepared with impregnating solutions having low pH values and containing a Group VIB metal component, a phosphorus component and citric acid, with the mole ratio of the citric acid to the Group VIB metal trioxide being greater than 0.1:1 but less than 0.5:1. The solutions contain dissolved phosphorus components, usually in a concentration greater than 0.5 weight percent but preferably greater than 1.0 weight percent, citric acid and Group VIB metal components, with the preferred Group VIB metals being molybdenum and tungsten, with molybdenum being most preferred. Preferably, the solution contains one or more Group VIB components in a total concentration of at least 3 weight percent, calculated as the metal trioxides, and more preferably in the range from about 5 to about 50 weight percent. The molar ratio of the citric acid to the Group VIB metal components (as the trioxide) in the solution is greater than about 0.1:1 but less than about 0.5:1. The solutions may also contain Group VIII metal components, especially cobalt or nickel, usually in a total concentration of at least 0.05 weight percent, usually at least 0.5 weight percent and preferably from about 1 to about 10 weight percent, calculated as the monoxide.

The presence of phosphorus in combination with citric acid in the impregnating solution utilized to prepare the final catalyst of this invention is required. Citric acid and phosphorus components are used to increase the activity of the finished hydroprocessing catalyst prepared from the impregnating

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solution when citric acid is added in such an amount that the mole ratio to the Group VIB metal component is greater than 0.1:1 but less than 0.5:1. Citric acid may be added to the solution in liquid or solid form. A preferred compound is citric acid monohydrate, although any suitable form of citric acid or its precursor may be utilized. As demonstrated in the examples hereafter, a catalyst of the invention prepared with the impregnating solution containing phosphorus and having a mole ratio of citric acid to a Group VIB metal trioxide (MoO_3) of greater than 0.1:1 but less than 0.5:1 is more active when utilized to promote denitrogenation reactions in hydrocarbon oils than is essentially the same catalyst except prepared from an impregnating solution containing no citric acid or containing citric acid at a mole ratio to a Group VIB metal trioxide more than 0.5:1.

The impregnating solution of the invention may be most conveniently prepared by dissolving into water a Group VIB metal compound, a compound containing phosphorus, citric acid, and optionally, a Group VIII metal component. The resulting solution has a pH less than about 1.0, and preferably from about 0 to less than 1.0. Generally, either the citric acid, phosphorus-containing compound or Group VIB metal compound is first dissolved in the aqueous medium under conditions which will effect dissolution and provide the specified concentrations of components. At atmospheric pressure, any temperature in the range of about 35° F. to about 210° F. may be employed, but it is generally preferred to use a temperature of about 75° F. to about 150°C.

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Preferably, the Group VIB metal component is first dissolved in water to form a slurry wherein at least about one milliliter of water

1 is utilized per gram of the compound containing the Group
2 VIB metal component. Typically, the phosphorus-containing
3 compound is an acid of phosphorus, such as the ortho-phos-
4 phoric acid (H_3PO_4) or a phosphoric acid precursor, that is
5 added to the aqueous slurry or solution in an amount that
6 effects dissolution of the phosphorus-containing compound
7 and the compound containing the Group VIB metal component.
8 The amount of phosphorus-containing compound (calculated
9 as P) needed to effect dissolution of the Group VIB metal
10 component is usually at least 10 percent of the weight of
11 the Group VIB metal component (calculated as the trioxide),
12 found in the finished hydroprocessing catalyst prepared from
13 the impregnating solution.

14 It is also preferred that the citric acid be added
15 to the solution after dissolution of at least a portion of
16 the Group VIB metal component, especially when an impreg-
17 nating solution is desired that contains a relatively large
18 proportion of Group VIB metal components, typically in a
19 total concentration greater than about 10 weight percent,
20 and particularly when greater than about 17 weight percent.
21 In addition to lowering the pH of an aqueous solution, it
22 is believed the presence of citric acid in the impregnating
23 solution improves the dispersion of a given amount of Group
24 VIB metal component on the surface area of the support par-
25 ticles and, more importantly, allows reduction of the total
26 amount of phosphorus components which are required to be
27 dissolved in the impregnating solution to effect Group VIB
28 metal component dissolution.

29 A variety of Group VIB metal components may be
30 utilized to produce a stable impregnating solution of the
31

1 invention. In general, all Group VIB metal compounds solu-
2 ble in aqueous media, particularly those of molybdenum or
3 tungsten, may be utilized. The oxides of molybdenum (e.g.,
4 molybdenum trioxide) are preferred, as are many salts con-
5 taining molybdenum, particularly precursors of molybdenum
6 trioxide. Also useful are salts containing both a Group VIB
7 metal and ammonium ion, such as ammonium dimolybdate, and
8 most preferably ammonium heptamolybdate.

9 After dissolution of the Group VIB metal, phos-
10 phorus-containing compound and citric acid, a Group VIII
11 metal component is then preferably added to the impregnating
12 solution. Suitable Group VIII metal compounds are water-
13 soluble, and usually include an oxide, carbonate, and pref-
14 erably a nitrate of cobalt, nickel, and iron, or combina-
15 tions thereof. The nitrates of cobalt and nickel are pre-
16 ferred, with nickel nitrate most preferred. Preferably,
17 the final solution contains Group VIII components (as the
18 monoxide) in a total concentration between about 1 and 10
19 weight percent and more preferably less than 6 weight per-
20 cent.

21 After addition of a Group VIII compound, the pH of
22 the solution may drop below about 1.0, but if the solution
23 remains above about 1.2, more acid is usually added to lower
24 the pH preferably below about 1.2, and more preferably below
25 about 1.0, and most preferably below about 0.8. The acid
26 used to lower the pH may be any acid containing thermally
27 decomposable anions or anions not resulting in undesirable
28 compounds in the final catalyst. Citric acid or phosphoric
29 acid is, of course, preferred, but others such as dilute
30 nitric acid, dilute sulfuric acid, dilute hydrochloric acid,
31

1 depending upon the final catalyst composition desired, may
2 be suitable to lower the pH.

3 Since the dissolved phosphorus-containing compound
4 is usually strongly acidic (i.e., phosphoric acid), the
5 presence of relatively large amounts thereof in the impreg-
6 nating solution may cause an undesirable reduction in the
7 pH of the solution that results in physical or chemical
8 degradation of the support particles utilized in the prep-
9 aration of the catalyst. Physical degradation of the sup-
10 port particles may result in a decrease in surface area
11 available for deposition of the Group VIB metal components
12 from the impregnating solution and/or the formation of ex-
13 cessive aluminum phosphate (AlPO_4) when the support parti-
14 cles contain aluminum. Excessive phosphorus (i.e., phos-
15 phoric acid) may also cause chemical degradation wherein an
16 undesirable amount of Group VIII metal aluminate (such as
17 NiAlO_4) may form during calcination due to undesirable or
18 excessive peptizing of the support (i.e., interaction with
19 excess hydroxyl groups on the support surface) thus causing
20 destruction of the preferred oxide form of the Group VIII
21 metal component after calcination. Accordingly, the phos-
22 phorus content in the impregnating solution must be con-
23 trolled by addition of citric acid in the amounts disclosed
24 herein.

25 One unusual feature of the invention is that the
26 impregnating solution is stable even when containing a
27 relatively large proportion of Group VIB metal components,
28 i.e., in a total concentration greater than about 10 weight
29 percent and preferably greater than 17 weight percent. Es-
30 sentially no crystalline deposits or crystalline aggregations
31

1 are detected in the impregnating solution of the invention
2 that result in a lessening in catalytic activity in the
3 final catalyst.

4 Several conventional methods may be employed to
5 impregnate the catalytic support particles with the solution
6 of this invention. One such method, commonly referred to as
7 the spray impregnation technique, involves spraying the sup-
8 port with the impregnating solution. Another impregnating
9 method, often used to maintain relatively low concentrations
10 of active components in the solution, is the circulation or
11 multi-dip procedure wherein the active support is repeatedly
12 contacted with the impregnating solution with or without in-
13 termittent drying. In order to take advantage of the dis-
14 persion property of the citric acid in the combination with
15 the phosphorus-containing compound and also the stability of
16 the solution of the invention (especially when relatively
17 high concentrations of Group VIB metals are desired), other
18 methods involving soaking the support in a large volume of
19 the impregnating solution or circulating the support therein
20 are preferred, as for example, the pore volume or pore sat-
21 uration technique, the continuous solution impregnation
22 (CSI) technique and the like. The pore saturation method
23 involves dipping the catalyst support into an impregnating
24 solution having a volume usually sufficient to fill the
25 pores of the support and, on occasion, may be up to about
26 10 percent excess. The concentrations of active components
27 in the solution during impregnation by this technique may be
28 somewhat higher than those utilized in other methods because
29 the ratios of active components in the final catalyst are
30 determined directly by solution composition.

1 The impregnating solution of the invention may be
2 utilized to incorporate the catalytically active components
3 with any of a number of porous refractory support particles.
4 Support particles suitable for use herein include such po-
5 rous, amorphous refractory oxides as silica, magnesia, sil-
6 ica-magnesia, zirconia, silica-zirconia, titania, silica-
7 titania, alumina, silica-alumina, etc. with supports con-
8 taining gamma, theta, delta and/or eta alumina being highly
9 preferred. Gamma alumina is the most highly preferred sup-
10 port. Other suitable porous refractory supports include
11 natural and synthetic crystalline and amorphous alumino-
12 silicates and crystalline silicas, e.g., silicalite. Pre-
13 ferred support particles having the preferred physical
14 characteristics disclosed herein are commercially avail-
15 able from Nippon-Ketjen Catalyst Division of AKZO-Chemie,
16 and American Cyanamid, Inc. Mixtures of the foregoing
17 oxides are also contemplated, especially when prepared as
18 homogeneously as possible.

19 The porous refractory oxide support material is
20 usually prepared in the form of shaped particulates, with
21 the preferred method being to extrude a precursor of the
22 desired support through a die having openings therein of
23 desired size and shape, after which the extruded matter is
24 cut into extrudates of desired length. The support parti-
25 cles may also be prepared by mulling (or pulverizing) a
26 precalcined porous refractory oxide to a particle size less
27 than about 100 microns and extruding the material.

28 The support particles prepared in the form of gel
29 extrudates are generally pre-calcined prior to impregnation,
30 especially if gamma alumina is the desired support material.

1 Temperatures above about 900° F. are required to convert the
2 alumina gel to gamma alumina. Usually, temperatures above
3 about 1,100° F. are utilized to effect this transformation,
4 with holding periods of one-half to three hours generally
5 being utilized to produce preferred gamma alumina extru-
6 dates.

7 The extruded particles may have any cross-sec-
8 tional shape, i.e., symmetrical or asymmetrical, but most
9 often have a symmetrical cross-sectional shape, preferably
10 a cylindrical or polylobal shape. The cross-sectional di-
11 ameter of the particles is usually about 1/40 to about 1/8
12 inch, preferably about 1/32 to about 1/12 inch, and most
13 preferably about 1/24 to about 1/15 inch. Among the pre-
14 ferred catalyst configurations are cross-sectional shapes
15 resembling that of a three-leaf clover, as shown, for ex-
16 ample, in Figures 8 and 8A of U.S. Patent 4,028,227. Pre-
17 ferred clover-shaped particulates are such that each "leaf"
18 of the cross-section is defined by about a 270° arc of a
19 circle having a diameter between about 0.02 and 0.05 inch.
20 Other preferred particulates are those having quadralobal
21 cross-sectional shapes, including asymmetrical shapes, and
22 symmetrical shapes such as in Figure 10 of U.S. Patent
23 4,028,227. Other particulates are available from Davison
24 Chemical Company, a division of W. R. Grace & Company, hav-
25 ing ring and minilith shapes, as disclosed in U.S. Patent
26 4,510,261.

27 The amounts of active components retained on the
28 support particles during impregnation will depend largely
29 on physical characteristics of the support particles, inter
30 alia, surface area, pore volume and pore size distribution.
31

1 Broadly speaking, the support particles have a surface area
2 of about 10 to about 400 m²/gram and typically above 100
3 m²/gram, and preferably about 125 m²/gram to about 400
4 m²/gram (as measured by the B.E.T. method). The total pore
5 volume of the amorphous support, as measured by conventional
6 mercury porosimeter methods, is usually about 0.2 to about
7 2.0 cc/gram, preferably about 0.25 to about to about 1.0
8 cc/gram, and most preferably about 0.3 to about 0.9 cc/gram.
9 The amorphous support particles may have essentially any
10 pore size distribution over a range of pore diameters as
11 small as about 25 angstroms to as large as about 10,000 ang-
12 stroms. Selection of a particular pore size distribution of
13 the support particles depends in large part on the particu-
14 lar hydroprocessing reaction that is to be promoted by the
15 final catalyst. For example, if demetallization of a re-
16 siduum oil is desired, the support particles are selected
17 with a pore size distribution such that the final catalyst
18 has at least about 5 percent of the pore volume in pores
19 having a diameter greater than 100 angstroms and preferably
20 an average pore diameter from about 50 to about 250 ang-
21 stroms. On the other hand, a pore size distribution of
22 support particles utilized to produce a final catalyst ef-
23 fective for desulfurization or denitrogenation of gas oils
24 should include pore sizes such that the final catalyst has
25 at least about 50 percent of the pore volume in pores having
26 a diameter from about 50 to about 150 angstroms. Physical
27 characteristics of three preferred amorphous refractory
28 oxide supports utilized in preparation of catalysts of the
29 invention are summarized in Table A as follows:

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TABLE A

<u>Pore Diameter Angstroms</u>	<u>Support X % Pore Volume</u>	<u>Support Y % Pore Volume</u>	<u>Support Z % Pore Volume</u>
40-50	-	-	4.0
<50	0.8	-	-
50-60	5.7	4.0	16.0
60-70	16.4	15.0	46.0
70-80	29.9	61.0	28.0
>80	-	-	6.0
80-90	24.6	13.0	-
>90	-	7.0	-
90-100	9.8	-	-
100-110	6.6	-	-
110-120	1.6	-	-
120-130	0.8	-	-
>130	5.7	-	-
PORE VOLUME cc/gram (Merc. Poros.)	0.61	0.63	0.58
MODE PORE DIAMETER, A (Merc. Poros.)	88	76	67
SURFACE AREA m ² /gram (B.E.T. method)	250	290	300

After impregnation, the support is dried and calcined to produce a catalyst containing the active components in desired proportions. The impregnated support particles may be dried and then calcined at a temperature of at least 750° F., and preferably from about 700° F. to about 1,400° F.,

1 so as to convert the active metals to their oxide forms.
2 However, impregnated support particles containing a signif-
3 icant portion of nickel are calcined at a temperature pref-
4 erably less than about 1,000° F., although support particles
5 containing significant amounts of cobalt may preferably be
6 calcined up to about 1,400° F. Furthermore, when calcining
7 support particles impregnated with a solution of the inven-
8 tion containing a Group VIII metallic nitrate, flowing air
9 is usually passed at a sufficient rate over the support par-
10 ticles to remove both the nitrogen oxide (NO and NO₂) and
11 carbon dioxide (CO₂) produced by the exothermic reactions
12 associated with nitrate and citric acid component decompo-
13 sition.

14 Calcination of the impregnated support particles
15 results in a substantial portion of the citric acid being
16 removed by decomposition. However, trace amounts of carbon
17 may remain after calcination and generally the final compo-
18 sition contains less than 0.5, preferably less than 0.1,
19 and most preferably 0 weight percent carbon, calculated as
20 C.

21 Another unusual feature of the invention is that,
22 after calcination of the impregnated support particles, no
23 crystalline deposits or crystalline aggregations resulting
24 in a lessening in activity or stability of the final cata-
25 lyst have been detected. Greater active component uniform-
26 ity in the catalytic particles typically improves activity.
27 The formation of a more evenly distributed layer of the
28 active components, such as the metals and their oxides, or
29 sulfides, in sufficient concentration throughout the sur-
30 face area of the catalytic support ordinarily provides more
31

1 provides more efficient utilization of the catalytic contact-
2 ing surface. Better dispersed forms of active components
3 onto the support particles from the impregnating solution
4 containing both citric acid and phosphorus are believed
5 responsible at least in part for the improved activity of
6 the catalysts of the invention as compared to conventional
7 catalysts. Impregnation of support particles with the so-
8 lution of the invention reduces the segregation of catalytic
9 components into inactive crystalline species on the support.

10 The final composition of the catalyst of the in-
11 vention contains a Group VIB metal component and a phos-
12 phorus component and, optionally, a Group VIII metal compo-
13 nent on the support particles. The physical characteristics
14 of the final catalyst composition will usually vary from
15 those of the support particles by less than about 25 per-
16 cent. The final composition generally contains at least
17 about 3 and preferably between about 5 and about 50 weight
18 percent Group VIB metal components, calculated as the tri-
19 oxides, and at least about 0.5 and preferably between 0.5
20 and 5 weight percent of phosphorus components, calculated
21 as P. If present, the finished catalyst contains from about
22 0.5 to about 10 weight percent, and usually about 2 to about
23 6 weight percent, of Group VIII metal components, calculated
24 as the monoxide. A highly preferred catalyst useful herein
25 contains about 17 to about 27 weight percent of Group VIB
26 metal components, calculated as the trioxide, from about 0.5
27 to about 5 weight percent of Group VIII metal components,
28 calculated as the monoxide, and about 1 to about 4 weight
29 percent of phosphorus components, calculated as P.

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1 It is also preferred, for desulfurization or de-
2 nitrogenation purposes, that the final catalyst composition
3 contain greater than 10 weight percent, and most preferably
4 between about 17 and about 30 weight percent of Group VIB
5 metal components, preferably about 1 to about 4 weight per-
6 cent of phosphorus components and preferably less than about
7 6 weight percent, and most preferably between about 1 and
8 about 5 weight percent Group VIII metal components. For
9 example, a catalyst composition comprises about 17 to about
10 30 weight percent of molybdenum components, about 0.5 to
11 about 5 weight percent of phosphorus components and from
12 about 1 to about 6 weight percent of nickel or cobalt com-
13 ponents, and has a surface area of about 100 to about 400
14 m²/gram, a pore volume of about 0.15 to about 1.2 cc/gram,
15 and a pore size distribution including at least 50 percent
16 of the total pore volume in pores of diameter between about
17 50 and about 150 angstroms.

18 In another preferred embodiment in which the cat-
19 alyst is utilized to promote demetallization reactions in a
20 residuum feedstock, the final composition contains about 3
21 to about 17 weight percent of Group VIB metal components,
22 calculated as MoO₃, up to about 5 weight percent of Group
23 VIII metal components, calculated as the monoxide, and up to
24 about 4 weight percent of phosphorus components, calculated
25 as P. The impregnating solution utilized to prepare such a
26 catalyst typically has a mole ratio of citric acid to MoO₃
27 greater than 0.5 to 1 and usually in the range from about
28 0.5 to 1 to about 1 to 1. For example, the catalyst con-
29 tains about 3 to about 17 weight percent of molybdenum
30 components, up to about 4 weight percent of phosphorus
31

1 components and up to about 3 weight percent of cobalt or
2 nickel components, and has a surface area of about 25 to
3 about 300 m²/gram, a pore volume of about 0.4 to about 1.5
4 cc/gram, and a pore size distribution including at least 5
5 percent of the total pore volume in pores of diameter great-
6 er than 100 angstroms. A highly preferred catalyst has a
7 mode pore diameter from about 135 to about 165 angstroms.

8 Ordinarily, a preferred hydroprocessing catalyst
9 is prepared from supports such as those disclosed herein in
10 Table A so as to have a narrow pore size distribution where-
11 in at least about 75 percent, preferably at least about 80
12 percent, and most preferably at least about 85 percent of
13 the total pore volume is in pores of diameter from about 50
14 to about 130 angstroms. Ordinarily the catalyst (such as a
15 catalyst prepared from Support X in Table A) has less than
16 about 10 percent of the total pore volume in pores of di-
17 ameter below about 50 angstroms and preferably less than
18 about 10 percent or 0.05 cc/gram of the pore volume in pores
19 of diameter greater than about 130 angstroms. The final
20 catalyst preferably has less than about 0.05 cc/gram or less
21 than about 10 percent of the total pore volume in pores of
22 diameter greater than about 110 angstroms (such as a cata-
23 lyst prepared from Supports Y or Z in Table A).

24 Another porosity feature of a preferred catalyst
25 of the invention is the narrow pore size distribution of the
26 pores of diameter greater than the mode pore diameter. (The
27 mode pore diameter, as referred to herein, is the pore di-
28 ameter represented on a pore size distribution curve of a
29 catalyst or support at which the derivative of the total
30 pore volume plotted on the ordinate vs. the pore diameter
31

1 plotted on the abscissa is a maximum.) The mode pore diam-
2 eter of the catalyst usually lies in the range from about
3 50 to about 115 angstroms, preferably 55 to about 100 ang-
4 stroms, and most preferably about 60 to about 90 angstroms.
5 Ordinarily, at least about 40 percent of the total pore
6 volume is in pores of diameter between the mode pore diam-
7 eter and less than about 90 angstroms, preferably less than
8 about 50 angstroms, and most preferably less than about 25
9 angstroms above the mode pore diameter. With respect to
10 small pores, at least about 40 percent of the total pore
11 volume is in pores of diameter between the mode pore diam-
12 eter and less than about 50, and preferably less than about
13 25 angstroms below the mode pore diameter.

14 One highly preferred catalyst employed in the in-
15 vention contains about 1 to about 6 weight percent of Group
16 VIII metal components, calculated as the monoxide, from
17 about 17 to about 35 weight percent of Group VIB metal com-
18 ponents, calculated as the trioxide, and about 1 to about 6
19 weight percent of phosphorus components, calculated as P, on
20 a porous refractory oxide support consisting essentially of
21 gamma alumina (such as Support X in Table A). The most pre-
22 ferred Group VIII and Group VIB metals in this embodiment
23 are cobalt and molybdenum, respectively. Physical charac-
24 teristics of this catalyst include a total pore volume of
25 about 0.30 to about 0.50 cc/gram, a surface area from about
26 125 to about 225 m²/gram and a mode pore diameter from about
27 80 to about 110 angstroms.

28 Another highly preferred catalyst prepared from
29 supports such as Y and Z in Table A contains about 1 to
30 about 6 weight percent of nickel component, calculated as
31

1 NiO, from about 17 to about 30 weight percent of molybdenum
2 components, calculated as MoO_3 , and about 1 to about 6
3 weight percent of phosphorus components, calculated as P,
4 on a support containing gamma alumina. This catalyst has a
5 surface area from about $125 \text{ m}^2/\text{gram}$ to about $250 \text{ m}^2/\text{gram}$, a
6 mode pore diameter from about 60 to about 90 angstroms, and
7 preferably about 70 to about 85 angstroms, and a pore size
8 distribution wherein less than 10 percent of the pore volume
9 is in pores of diameter greater than 110 angstroms. It is
10 also preferred that this catalyst contain at least about 70
11 percent of the pore volume in pores of diameter in the range
12 from about 20 angstroms above and about 20 angstroms below
13 the mode pore diameter. As shown hereinafter in Example I,
14 a highly preferred catalyst embodiment contains less than 25
15 and preferably about 22 to about 24.5 weight percent of mo-
16 lybdenum components, less than 4.5 and preferably about 2 to
17 about 3.8 weight percent of nickel components and less than
18 3 and preferably about 1.5 to about 2.8 weight percent of
19 phosphorus components, calculated as P.

20 After calcination, the final catalyst is generally
21 activated by conventional means for its intended use in a
22 given hydroprocess of a hydrocarbon oil. The catalyst may,
23 for example, be activated by reduction of the active compo-
24 nents to the free metal form, employed in the calcined oxide
25 form or conversion of the oxide form to the sulfide form.
26 When employed with active components in the sulfide form,
27 the catalyst may be presulfided so as to convert the ac-
28 tive metal components to the corresponding sulfides. Usu-
29 ally the catalysts are presulfided prior to use by contact
30 with a stream of sulfiding gas, such as hydrogen sulfide-
31

1 hydrogen mixtures containing about 1 to 10 volume percent of
2 hydrogen sulfide, at temperatures between about 200° F. and
3 1,200° F. Although presulfiding of the catalyst is pre-
4 ferred, it is not essential, as the catalyst may be sulfid-
5 ed "in situ" in a short time by contact with a sulfur-con-
6 taining feedstock processed under hydroprocessing condi-
7 tions.

8 The catalyst of this invention may be employed in
9 any of several processes for hydroprocessing hydrocarbon-
10 containing oils wherein catalytic composites containing
11 Group VIB metals and phosphorus components, or Group VIB
12 and Group VIII metals and phosphorus components are known
13 to be catalytically effective, such as hydrogenation, de-
14 hydrogenation, hydrodesulfurization, oxidation, hydrode-
15 nitrogenation, hydrodemetallization, hydroisomerization,
16 hydrocracking, mild hydrocracking, hydroreforming, and the
17 like. Contemplated for treatment by the process of the in-
18 vention are relatively high boiling hydrocarbon-containing
19 oils including crude petroleum oils and synthetic crudes.
20 Among the typical oils contemplated are top crudes, vacuum
21 and atmospheric residual fractions, light and heavy atmos-
22 pheric and vacuum distillate oils, deasphalted oils, shale
23 oils, and oils from bituminous sands, coal compositions and
24 the like. For use herein, typical hydrocarbon oils, or mix-
25 tures thereof, may contain at least about 10 volume percent
26 of components normally boiling above about 1000° F. and in
27 some cases, at least 20 volume percent. Other hydrocarbon
28 oils include lubricating oils, waxes, kerosene, solvent
29 naphthas, fuel oils, diesel fuels, jet fuels, heavy naph-
30 thas, light naphthas, cycle oils from cracking operations,

1 coker distillates, cracked gasoline, decant oils, and the
2 like.

3 Generally, a substantial proportion (i.e., at
4 least about 90 volume percent) of hydrocarbon feeds such as
5 gas oils and the like boil at a temperature less than about
6 1100° F., preferably less than about 1050° F., and usually
7 boil entirely within the range of about 100° F. to about
8 1100° F., and most frequently in the range from about 400°
9 F. to about 1100° F.

10 Although virtually any high boiling hydrocarbon
11 feedstock may be treated by hydroprocessing with the cata-
12 lyst of the invention, the process is particularly suited to
13 treating (1) gas oils, preferably light and heavy vacuum gas
14 oils and waxy shale oils, and (2) heavy residual fractions,
15 especially the treated atmospheric and vacuum residuum oils
16 containing less than about 25 ppmw, preferably less than 5
17 ppmw and most preferably less than 3 ppmw of contaminant
18 metals (vanadium, nickel, and the like). Sulfur is usually
19 present in such oils in a proportion exceeding 0.1 weight
20 percent and often exceeding 1.0 weight percent; however, a
21 particular preferred proportion is about 0.1 to about 0.5
22 weight percent. The feedstock contains undesirable propor-
23 tions of nitrogen, usually in a concentration greater than
24 about 2 ppmw and often between about 2 ppmw and 5000 ppmw.
25 Ordinarily the feedstock contains less than 200 ppmw of
26 nickel and vanadium contaminant metals, calculated as Ni
27 plus V, with preferred feedstocks containing less than 20
28 ppmw and most preferably less than 5 ppmw of said materials.
29 The feedstock may contain waxy components, e.g., n-paraffins

1 and slightly-branched paraffins, and thus have a high pour
2 point, e.g., at least about 30° F.

3 The catalyst may be employed as either a fixed,
4 ebullating, slurried or fluidized bed (but most usually a
5 fixed bed) of particulates in a suitable reactor vessel
6 wherein the hydrocarbon oil to be treated is introduced
7 and subjected to hydroprocessing conditions including an
8 elevated total pressure, temperature, and hydrogen partial
9 pressure. Under such conditions, the hydrocarbon oil and
10 catalyst are subjected to a hydrogen partial pressure usu-
11 ally in the range from about 100 to about 4,000 p.s.i.g.
12 at a space velocity usually in the range from about 0.05 to
13 about 20 LHSV so as to effect the desired degree of hydro-
14 processing, as for example, demetallization, desulfurization
15 and/or denitrogenation, i.e., so as to effect the desired
16 degree of conversion of, for example, sulfur, nitrogen and
17 metal-containing compounds to hydrogen sulfide, ammonia,
18 and metal forms capable of being deposited in the catalyst,
19 respectively. The catalyst of the invention is particular-
20 ly effective for desulfurization, denitrogenation and de-
21 metallization reactions, especially when utilized to process
22 hydrocarbon oils such as gas oils and residuum fractions.

23 In the hydroprocessing of a hydrocarbon oil, the
24 catalyst is usually maintained in a hydroprocessing reactor
25 as a fixed bed with the feedstock passing downwardly once
26 therethrough. In some instances, one or more additional
27 reactors may be added to the single reactor, either in se-
28 ries or parallel. If the feedstock is unusually high in
29 organometallic compounds, it may be pretreated, integral-
30 ly or separately, using a conventional hydrodemetallation

1 catalyst or a hydrodemetallation catalyst of the invention
2 and particularly, a hydrodemetallation catalyst having a
3 substantial amount of pore volume in pores of diameter great-
4 er than that corresponding to the average pore volume of the
5 catalyst of the invention.

6 Typical hydroprocessing conditions that are suit-
7 able for hydrodenitrogenation, hydrodesulfurization, or that
8 yield more than about 10 volume percent conversion of the
9 oil fraction boiling above 1000° F. to liquid products boil-
10 ing at or below 1000° F. are shown in the following Table I:

11 TABLE 1

13 <u>Operating Conditions</u>	<u>Suitable Range</u>	<u>Preferred Range</u>
14 Temperature, °F.	500 - 900	600 - 850
15 Hydrogen Pressure, p.s.i.g.	200 - 4,000	500 - 2,500
16 Space Velocity, LHSV	0.05 - 5.0	0.1 - 3.0
17 Hydrogen Recycle Rate, scf/bbl	500 - 15,000	1,000 - 10,000

18
19 Generally, the hydrogen partial pressure maintain-
20 ed during hydroprocessing is more than 50 percent of the to-
21 tal pressure. Usually, for once-through operation, the hy-
22 drogen partial pressure is between about 85 and 95 percent
23 of the total pressure while, for recycle operation, the hy-
24 drogen partial pressure is somewhat lower, i.e., between 80
25 and 85 percent of the total pressure.

26 The hydroprocess of the invention may include
27 either serial or simultaneous desulfurization and denitro-
28 genation of a feedstock. Simultaneous desulfurization, de-
29 nitrogenation and heavy component (1000° F. plus components)

1 conversion, as used herein, involves contacting a hydrocar-
2 bon oil feedstock with the particulate catalyst disclosed
3 herein under conditions effecting (1) a lower sulfur and
4 nitrogen content in the effluent and (2) a higher percent-
5 age of liquid products boiling at or below 1000° F. in the
6 effluent as compared to the feedstock. Serial desulfuriza-
7 tion and denitrogenation of a feedstock by contact with the
8 catalyst of the invention involves removing sulfur and ni-
9 trogen from the feedstock either prior to or after contact
10 of the feedstock with a catalyst effective for removing a
11 substantial proportion of contaminant metals from the feed.

12 A preferred embodiment utilizing the catalyst of
13 the invention comprises a combined hydrodemetallation, hy-
14 drodesulfurization and hydrodenitrogenation reaction zone
15 wherein the catalyst of the invention is located in a down-
16 stream portion of a fixed bed relative to an upstream cata-
17 lyst bed portion containing a demetallation catalyst having
18 an average pore diameter of at least 30 angstroms greater
19 than that of the catalyst of the invention. In contrast to
20 utilizing a comparable narrow pore sized catalyst prepared
21 without citric acid in the impregnating solution, or more
22 particularly without citric acid in a mole ratio to MoO_3 of
23 less than 1 to 1, in the downstream location of the catalyst
24 bed, the catalyst of the invention exhibits better activity
25 and provides a surprisingly more stable process for removing
26 nitrogen, sulfur and conversion of 1000° F. plus components
27 to 1000° F. minus components in the oil.

28 The invention is further illustrated by the fol-
29 lowing examples which are illustrative of specific modes of
30

1 practicing the invention and are not intended as limiting
2 the scope of the invention as defined in the appended claims.

3
4 EXAMPLE I

5 A catalyst, Catalyst A, prepared in accordance
6 with the invention is tested under typical hydrodesulfuri-
7 zation conditions against a reference catalyst, Catalyst X.
8 Catalysts A and X have a 1/20 inch trilobal cross-sectional
9 shape and have nominal compositions of 25.0 weight percent
10 of molybdenum components, calculated as MoO_3 , 4.0 weight
11 percent of nickel components, calculated as NiO , 3.0 weight
12 percent of phosphorus, calculated as P, and the balance of
13 gamma alumina. Catalyst A of the invention is prepared as
14 follows:

15 An impregnating solution of the invention is pre-
16 pared by placing 47 grams of ammonium heptamolybdate (AHM)
17 in a beaker containing 47 ml of water and partially dis-
18 solving AHM by stirring for one minute. Undissolved AHM
19 is dissolved by stirring into the resulting solution about
20 17 grams of 85 percent phosphoric acid (H_3PO_4). After dis-
21 solution of the AHM, 14 grams of citric acid (monohydrate)
22 is dissolved in the resulting solution to provide a mole
23 ratio of 0.2 to 1, citric acid (calculated as the mono-
24 hydrate) to AHM (calculated as MoO_3). Nickel nitrate
25 ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in the amount of 24 grams is then dissolved
26 in the resulting solution. After dissolution of the nickel
27 nitrate, an impregnating solution having a volume of 70 ml
28 and a pH of about 0.3 is obtained. This solution is stable
29 and may be stored for two weeks or longer prior to impreg-
30 nation.

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1 Gamma alumina support particles (100 grams), hav-
2 ing a pore size distribution as shown in Table II, are then
3 contacted with the impregnant solution. Substantially all
4 70 ml of the impregnant solution is taken up by the support.

5 The impregnated composition is allowed to stand
6 (age) for two hours following which it is oven dried at 110°
7 C. and then calcined at 900° F. for 1/2 hour in flowing air.
8 The final catalyst has a pore size distribution as shown in
9 Table II. Catalyst X is prepared in the same manner and
10 from the same support as Catalyst A except no citric acid
11 is added to the impregnating solution.

TABLE II

PORE SIZE DISTRIBUTIONS AND SURFACE AREAS

	<u>Support</u>	<u>Catalyst A</u>
Pore Diameter, Angstroms	% of total p.v.	% of total p.v.
<40	0.9	0.6
40-50	1.8	1.8
50-60	10.0	3.5
60-70	36.4	9.8
70-80	34.0	20.6
80-90	7.8	30.3
90-100	1.0	18.0
100-110	1.8	7.4
>110	6.3	8.0
TOTAL PORE VOLUME (Merc. Poros.)	0.55	0.34
SURFACE AREA m ² /gram (B.E.T. method)	300	175
MODE PORE DIAMETER, Å (Merc. Poros.)	68	82

The test is conducted by contacting the catalysts in separate runs with the feedstock identified in Table III under hydroprocessing conditions. However, at the outset of each run, the respective catalysts are presulfided by contact for about 16 to 20 hours with a gas consisting of 90 volume percent H₂ and 10 volume percent H₂S flowing at 4.4 SCFM (one atmosphere pressure). The temperature during the

presulfiding is initially at room temperature, is increased gradually until 700° F. is reached, and then lowered to 550° F., at which time the catalyst is contacted with the feedstock.

TABLE III

Feedstock Properties

Feed Description	Vacuum Gas Oil
Gravity, °API	23.2
Sulfur, wt.%	1.8
Total Nitrogen, wt.%	0.312
Basic Nitrogen, wt.%	0.129
Pour Point, °C.	-18
ASTM D-1160, Vol.%	Distillation, °F.
IBP/5	185/520
10/20	542/577
30/40	605/633
50/60	667/691
70/80	719/742
90/95	771/796
End Point	817

A portion of the feedstock is passed downwardly through a reactor vessel and contacted in separate runs with Catalyst A and Catalyst X, in a single-stage, single-pass system with once-through hydrogen. The operating conditions during each run are summarized as follows: 1,400 p.s.i.g. total pressure, 2.0 LHSV, a hydrogen rate of 6,000 SCF/bbl, and an initial temperature of 720° F.

Giving Catalyst X employed at 60 hours in the reference hydroprocess an arbitrary activity of 100, relative activities of Catalyst A of the invention and Catalyst X for denitrogenation and desulfurization are determined by calculation and tabulated in comparison to Catalyst X in Table IV. These denitrogenation activity determinations are based on a comparison of the reaction rates for denitrogenation obtained from the data of the experiment according to the following standard equation which assumes first order kinetics for denitrogenation:

$$\text{Relative Denitrogenation Activity} = \frac{\ln [C_f/C_p]}{\ln [C_{fr}/C_{pr}]} \times 100$$

where C_{fr} and C_{pr} are the respective concentrations of nitrogen in the feed and product obtained with the catalyst employed in the reference process and C_f and C_p are the respective concentrations of nitrogen in the feed and product obtained with a catalyst being compared to the reference.

These desulfurization activity determinations are based on a comparison of the reaction rates for desulfurization obtained from the data of the experiment according to the following standard equation which assumes one and one-half order kinetics for desulfurization:

$$\text{Relative Desulfurization Activity} = \frac{(1/S_p)^{1/2} - (1/S_f)^{1/2}}{(1/S_{pr})^{1/2} - (1/S_{fr})^{1/2}} \times 100$$

where S_{fr} and S_{pr} are the respective concentrations of sulfur in the feed and product obtained with the reference catalyst and S_f and S_p are the respective concentrations of sulfur in the feed and product obtained with a catalyst being compared to the reference.

The relative volume activity (RVA) for total nitrogen and sulfur conversion obtained for each catalyst is set forth in Table IV. The data in Table IV indicate that Catalyst A prepared from an impregnant solution containing citric acid in a mole ratio to MoO_3 of less than 1 to 1, is consistently more active (i.e., at least about 10 percent) than essentially the same catalyst prepared without citric acid in the impregnant solution.

TABLE IV

Catalyst	RVA for basic nit., $N_{(b)}$	for total nit., $N_{(t)}$	for sulfur, S
A	112	115	115
X	100	100	100

EXAMPLE II

Catalyst X of Example I and another catalyst of the invention, Catalyst B, are tested in separate runs for hydroprocessing the feedstock of Example I under the same conditions as Example I.

Catalyst B is prepared in the same manner as Catalyst A in Example I, except the AHM and phosphoric acid amounts are reduced. The citric acid (12 grams) is added in an amount providing a mole ratio of citric acid to MoO_3

1 of 0.2 to 1. The pH of the resulting impregnating solutions
2 is 0.35.

3 The dried and calcined finished catalyst has a
4 nominal composition as set forth in Table V.

6 TABLE V

7

Catalyst	<u>MoO₃</u>	<u>NiO</u>	<u>P</u>	<u>N_(b)</u>	<u>N_(t)</u>	<u>S</u>
8 X	25.0	4.0	3.0	100	100	100
9 B	23.9	3.5	2.6	124	123	133

10

11 The data in Table V indicate that Catalyst B,
12 containing less phosphorus and molybdenum components than
13 Catalyst X (or Catalyst A in Example I), is also more active
14 for denitrogenation and desulfurization than Catalyst X (or
15 Catalyst A in Example I).

16 While particular embodiments of the invention have
17 been described, it will be understood, of course, that the
18 invention is not limited thereto since many obvious modifi-
19 cations can be made, and it is intended to include within
20 this invention any such modifications as will fall within
21 the scope of the invention as defined by the appended claims.
22

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A catalytic composition prepared by the method comprising the steps of:
 - (1) impregnating support particles with an aqueous impregnating solution which has a pH less than 1.0 and comprises (a) one or more Group VIB metal components, (b) one or more phosphorus components and (c) citric acid in a mole ratio to the Group VIB metal components calculated as the Group VIB metal trioxide of greater than 0.1:1 but less than 0.5:1, and
 - (2) calcining the impregnated support particles.
2. The composition defined in claim 1, wherein the impregnating solution further comprises one or more Group VIII metal components.
3. The composition defined in claim 1, wherein the impregnating solution contains at least about 3 weight percent of the Group VIB metal components, calculated as the trioxide.
4. The composition defined in claim 1, wherein the impregnating solution contains at least about 1.0 weight percent of the phosphorus components, calculated as P.
5. The composition defined in claim 2, wherein the impregnating solution contains at least about 0.5 weight percent of the Group VIII metal components, calculated as the monoxide.

6. The composition defined in claim 5, wherein the Group VIII metal is nickel.

7. The composition defined in claim 5, wherein the Group VIII metal is cobalt.

8. The composition defined in any one of claims 1 to 5 comprising a weight percent of the phosphorus components, calculated as P, that is at least 10 percent of the weight percent of the Group VIB metal components, calculated as the trioxide.

9. The composition defined in claim 2 comprising at least about 17 weight percent of molybdenum components, calculated as MoO_3 , at least about 1.0 weight percent of phosphorus components, calculated as P, and at least about 0.5 weight percent of nickel components, calculated as NiO.

10. The composition defined in claim 9, wherein the support particles comprise at least 75 percent of the total pore volume in pores of diameter from about 50 to about 130 angstroms.

11. The composition defined in claim 9, wherein the support particles comprise at least 75 percent of its pore volume in pores of diameter from about 50 to about 110 angstroms and less than about 10 percent of the total pore volume in pores of diameter greater than 110 angstroms.

12. The composition defined in claim 2 comprising about 22 to about 24.5 weight percent of molybdenum components, calculated as MoO_3 , about 0.5 to less than 3 weight percent of phosphorus components, calculated as P, and 0.5 to less than 4.5 weight percent of nickel components, calculated as NiO.
13. An aqueous impregnating solution for preparing a catalyst composition, which solution has a pH less than 1.0 and comprises one or more dissolved Group VIB metal components, one or more phosphorus components and citric acid in a mole ratio to the Group VIB metal components greater than 0.1:1 but less than 0.5:1, calculated as citric acid to the Group VIB metal trioxide.
14. The solution defined in claim 13, further comprising one or more Group VIII metal components.
15. The solution defined in claim 14, wherein the phosphorus component comprises phosphoric acid.
16. The solution defined in claim 13 containing at least about 3 weight percent of the Group VIB metal components.
17. The solution defined in claim 13 containing at least about 17 weight percent of the Group VIB metal components.
18. The solution defined in claim 13 containing at least about 1.0 weight percent of the phosphorus components.
19. The solution defined in claim 14 containing at least about 0.5 weight percent of the Group VIII metal components.

20. The solution defined in claim 19 wherein the Group VIII metal is cobalt.

21. The solution defined in claim 19 wherein the Group VIII metal is nickel.

22. The solution defined in claim 13 wherein the Group VIB metal components comprise molybdenum.

23. The solution defined in claim 14 wherein the Group VIII metal components comprise cobalt or nickel.

24. The solution defined in claim 13 wherein the phosphorus components comprise phosphoric acid.

25. The solution defined in claim 13 wherein the phosphorus components, calculated as P, comprise at least 10 percent of the weight percent of the Group VIB metal components, calculated as the trioxide.

26. The solution defined in claim 13 comprising sufficient concentrations of the Group VIB metal components, of the phosphorus components, and of citric acid to provide a final catalytic composition comprising at least about 3 weight percent of the Group VIB metal components and at least about 0.3 weight percent of the phosphorus components.

27. The solution defined in claim 13 comprising sufficient concentrations of the Group VIB metal components, of the phosphorus components, of the Group VIII metal components, and of citric acid to provide a final catalytic composition comprising at least about 3 weight percent of the Group VIB

metal components, at least 0.5 weight percent of the Group VIII metal components and at least about 0.3 weight percent of the phosphorus components.

28. A catalytic composition containing about 22 to about 24.5 weight percent of Group VIB metal components, calculated as the trioxide, about 2 to about 4.5 weight percent of Group VIII metal components, calculated as the monoxide, and about 1.5 to about 2.8 weight percent of phosphorus components, calculated as P, prepared by the method comprising the steps (1) impregnating support particles with the aqueous impregnating solution of claim 13, and (2) calcining the impregnated support particles.

29. A catalytic composition prepared by the method comprising the steps of (1) impregnating support particles with the aqueous impregnating solution of claim 13, and (2) calcining the impregnated support particles.

30. A catalytic composition prepared by the method comprising the steps of (1) impregnating support particles with the aqueous impregnating solution of claim 26, and (2) calcining the impregnated support particles.

31. A catalyst composition containing about 17 to about 27 weight percent of Group VIB metal components, about 1.0 to about 4.0 weight percent of phosphorus components, and about 0.5 to about 5.0 weight percent of Group VIII metal components, prepared by the method comprising the steps of (1) impregnating support particles with the aqueous impregnating solution of claim 27, and (2) calcining the impregnated support particles.

32. The composition defined in claim 31 having a pore size distribution wherein at least 75 percent of the total pore volume is in pores of diameter from about 50 to about 130 angstroms and has a mode pore diameter from about 55 to about 100 angstroms.

33. The composition defined in claim 32 having less than 10 percent of the total pore volume in pores of diameter greater than 110 angstroms.

34. An impregnating solution for preparing a catalyst composition, which solution has a pH less than 1.0 and comprises one or more Group VIB metal components, one or more phosphorus-containing acids and citric acid in a mole ratio to the Group VIB metal components, calculated as the trioxide, in the range from greater than 0.1:1 but less than 0.5:1.

35. The solution defined in claim 34 further comprising one or more Group VIII metal components.

36. The solution defined in claim 35 wherein the Group VIII metal is cobalt or nickel.

37. The solution defined in claim 35 comprising a molybdenum component as the Group VIB metal component and cobalt or nickel component as the Group VIII metal component.

38. A catalyst composition prepared by a method employing the impregnating solution of claim 37.

39. The composition defined in claim 38 containing about 3 to about 17 weight percent of molybdenum components, calculated as MoO_3 , about 0.05 to about 4.0 weight percent of nickel or cobalt components, calculated as the monoxide, and has a pore size distribution including at least about 5 percent of the total pore volume in pores of diameter greater than 100 angstroms.

40. The composition defined in claim 39 having a mode pore diameter from about 135 to about 165 angstroms.

41. A method for preparing a catalyst composition comprising:

(1) preparing an aqueous impregnating solution having a pH of less than 1.0 by the following sequential steps: (a) at least partially dissolving one or more Group VIB metal components in water, (b) dissolving a compound of phosphorus and (c) dissolving citric acid in a mole ratio to the Group VIB metal components, calculated as the trioxide, of greater than 0.1:1 but less than 0.5:1,

(2) impregnating support particles with the solution of step (1), and

(3) calcining the impregnated support particles of step (2).

42. The method defined in claim 41 further comprising a step (d) wherein a Group VIII metal component is dissolved in the solution.

43. The method defined in claim 42 wherein the Group VIB metal components comprise molybdenum trioxide or ammonium heptamolybdate, the compound of phosphorus comprises phosphoric acid and the Group VIII metal components comprise cobalt nitrate or nickel nitrate.

44. The method defined in claim 41 wherein the Group VIB metal is molybdenum.

45. A catalytic hydroprocess of a hydrocarbon oil containing nitrogen or sulfur, said hydroprocess comprising contacting the catalytic composition of claim 1 with said hydrocarbon oil under hydroprocessing conditions so as to produce a product hydrocarbon oil containing less nitrogen or sulfur than said hydrocarbon oil.

46. A catalytic hydroprocess of a hydrocarbon oil containing contaminant metals, nitrogen or sulfur, said hydroprocess comprising contacting the catalytic composition of claim 39 with said hydrocarbon oil under hydroprocessing conditions so as to produce a product hydrocarbon oil containing less nitrogen, sulfur or contaminant metals than contained in said hydrocarbon oil.

47. A hydrocarbon hydroprocessing catalytic composition prepared by the method comprising the steps of (1) impregnating porous support particles of a refractory oxide with an aqueous impregnating solution which (a) comprises at least one Group VIB metal component in an amount of at least 3 weight percent but not more than 50 weight percent calculated as the metal trioxide, the Group VIB metal being selected from the class consisting of molybdenum and tungsten, (b) comprises at least

one dissolved acid of phosphorus in a concentration greater than 0.5 weight percent, (c) comprises citric acid in a molar ratio to the said Group VIB metal component calculated as the Group VIB metal trioxide in the range greater than 0.1:1 but less than 0.5:1, and (d) may also comprise at least one Group VIII metal component in a total concentration of not more than about 10 weight percent calculated as the monoxide, the Group VIII metal being selected from the class consisting of iron, cobalt and nickel, wherein the aqueous impregnating solution has a pH less than about 1.0 and (2) calcining the impregnated support particles under such conditions that the Group VIB metal and the Group VIII metal if any are in their oxide forms and citric acid is essentially decomposed after the calcination.

48. A method for preparing a hydrocarbon hydroprocessing catalyst composition comprising active components on porous support particles of a refractory oxide, the active components containing (A) at least one Group VIB metal component in an amount of at least 3 but not more than 50 weight percent, calculated as trioxide, the Group VIB metal being selected from the class

consisting of molybdenum and tungsten, (B) between 0.5 to 5 weight percent of a phosphorus component, calculated as P, (C) from 0 to 10 weight percent, calculated as monoxide, of at least one Group VIII metal component selected from the class consisting of iron, cobalt and nickel, which process comprises the steps of:

(1) impregnating the support particles with a stable aqueous impregnating solution which has a pH less than about 1.0 and comprises (a) from 3 to 50 weight percent of the Group VIB metal calculated as the trioxide, (b) at least one dissolved acid of phosphorus in a concentration of from 0.5 and 5 weight percent, (c) citric acid in a molar ratio to the said Group VIB metal component calculated as trioxide in the range greater than 0.1:1 but less than 0.5:1 and (d) the Group VIII metal component in a concentration of from 0 to 10 weight percent calculated as monoxide; and

(2) calcining the impregnated support particles under such conditions that, after calcination, the Group VIB metal and the Group VIII metal if any are in their oxide forms and citric acid is essentially decomposed, thereby obtaining the catalyst composition in which the metals are in the oxide form.

49. A method defined in claim 48, which further comprises reduction-activation of the metal oxides into their free metal forms, thereby obtaining the catalyst composition in which the metals are in the free metal form.

50. A method defined in claim 48, which further comprises presulfidation of the metal components into their corresponding

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sulfide forms, thereby obtaining the catalyst composition in which the metals are in the sulfide form.

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51. A method defined in claim 48, 49 or 50, wherein the refractory oxide is alumina; the Group VIB metal is molybdenum; the acid of phosphorus is phosphoric acid; and the Group VIII metal is employed and is nickel.

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